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ΠΡΟΕΔΡΙΑ ΛΟΥΚΑ ΜΟΥΣΟΥΛΟΥ

ΜΗΧΑΝΙΚΗ.— Polyetheretherketone (PEEK): A Matrix Semicrystalline Polymer for High Performance Composites, ὑπὸ *James C. Seferis**, διὰ τοῦ Ἀκαδημαϊκοῦ κ. Περικλῆ Θεοχάρη.

A B S T R A C T

The processing, structure and properties of polyetheretherketone (PEEK) semicrystalline thermoplastic as matrix polymer for high performance composites has been investigated in this work. In processing PEEK samples with different crystallinities, a specially designed mold capable of cooling the polymer in excess of 115°C/sec from its melt temperature was constructed. In addition, during processing studies, a reaction of PEEK in the presence of copper was discovered. Analysis of the samples in terms of their crystallinity values also provided a new method for measuring crystallinity of the matrix in the composite. Crystallization of low crystalline samples at room temperature in the presence of methylene chloride was also confirmed for the first time with polarized microscopy. However, at the same time, the excellent hygrothermal resistance of PEEK was also confirmed. Finally, dynamic mechanical and stress-strain experiments with samples of different crystallinities elucidated the dependence of these properties to crystallinity. However, this study also elucidated that under normal processing conditions for high performance composites, PEEK properties may not be strongly affected by different levels of crystallinity.

I N T R O D U C T I O N

High performance composite systems made up of a polymer reinforced with high strength and stiffness fibers such as carbon and Kevlar are being increasingly utilized in aerospace structures due to their offered weight sav-

* ΔΗΜΗΤΡΙΟΥ ΣΕΦΕΡΗ, Πολυμερῆ με ἡμικρυσταλλικὴν μήτρα κατάλληλα διὰ σύνθετα ὑλικά ὑψηλῆς ἀντοχῆς.

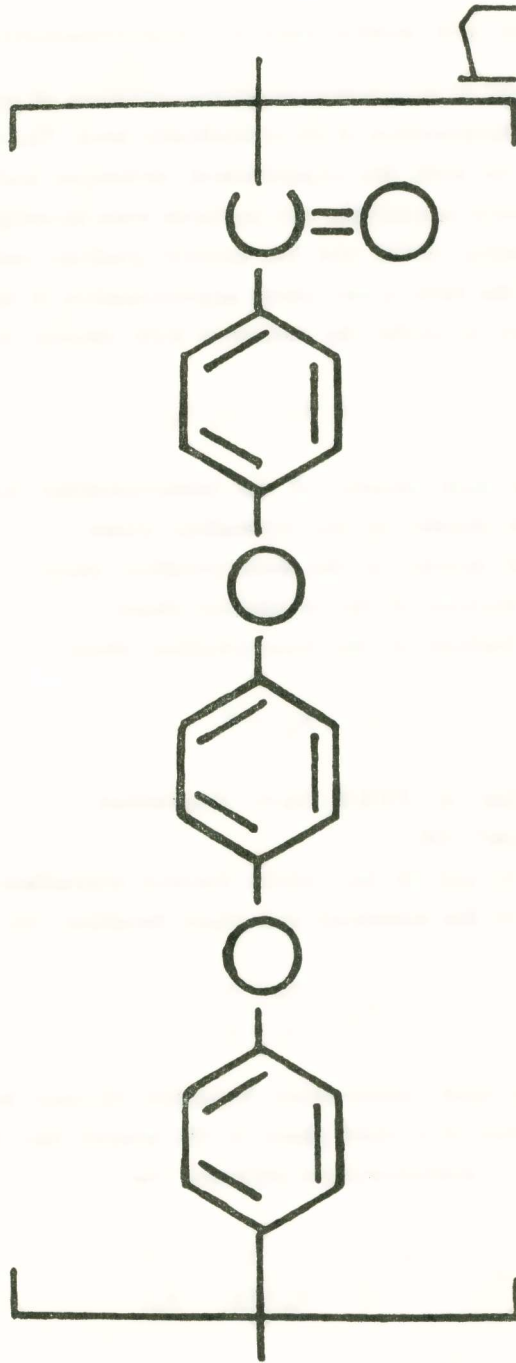
ings advantage over traditionally used metals such as aluminum and titanium. Although for decades it was assumed that the role of the matrix in fibrous composites was simply to transfer the load between the reinforcing fibers and to protect them during processing into useful shapes, it is beginning to be increasingly recognized that a vital role in performance is being played by the polymer matrix system employed (1). For high performance applications, thermosetting polymers have been utilized almost exclusively in composite systems. However, unlike the metals that the composites are replacing, the chemical composition, as well as the processing conditions employed, can all influence the final bulk properties of the matrix polymer. Thus, an investigation on how the processing conditions affect the properties of thermosetting polymer matrices is essential for improving our state of understanding of composites.

During the past several years, we have been developing techniques and model compounds approximating utilized epoxy matrix systems for high performance composites. Our work, along with other investigators, has begun to provide a fundamental understanding required for improvement and/or use of different polymers as matrix systems in fiber reinforced composites. For example, for the first time we observed that these highly utilized epoxy systems may not be completely reacted when processed into composites which may lead to different absorption of moisture levels during their usage [2, 3]. We have developed molecular models to explain data that suggested that these systems were heterogeneous, as a result of differences in crosslinking density throughout the system. However, we also established that different processing techniques, as well as different chemical species utilized, may alter these heterogeneities giving rise to different properties of the matrix polymer [4, 5, 6]. These processing studies led to a new understanding of how the kinetics of polymerization may lead to changes in the polymer's viscous behavior during composite manufacturing processes (7). All studies with thermosetting polymers were performed both with neat resins as well as composites, elucidating with a micromechanics approach the influence of the matrix on the composite properties (8). Thus, in general, we have been examining these composite systems as heterogeneous anisotropic polymers whose physical properties depend on their processing history that give rise to a specific molecular and supramolecular morphology. We have used, however, the same composite analogy for heterogeneous materials in analyzing the processing-

structure-property relations of crystalline polymers. Working with polyethylene and polypropylene as model systems, we have developed a composite methodology by which intrinsic properties of the crystalline and noncrystalline phases of the polymer could be identified irrespective of the polymer's previous history [9]. Application of this methodology enabled quantitative characterization of the morphological features of both phases of the polymer through infrared spectroscopy providing a uniform perspective of understanding [9, 10]. This structural information could in turn be used in the modelling methodology to predict seemingly diverse properties of the polymer like the dynamic mechanical and optical properties [11, 12].

When over the last few years interest in thermoplastics as matrix materials for improved toughness in high performance composites was increasing, it was only natural that we would begin to look into these new systems. Specifically, the polymer matrix material chosen for our studies as a model system was a semicrystalline polymer polyetheretherketone (PEEK) which has some unique properties. Its chemical structure and physical properties are shown in Figure 1. Although the polymer is commercially available from Imperial Chemical Industries (ICI) both in its neat form and reinforced with carbon fibers, very little is known concerning its processing, structure and properties [13, 14]. Thus, this system was ideally suited for us to apply and extend our analytical methodology for further testing and development.

This work summarizes our significant findings to date while we have been investigating the processing, structure and properties of PEEK (both in its neat form and in carbon reinforced composite form). In particular, although we had a broad background to build upon, based on previous findings and experience with the model crystalline polymers and thermosetting matrix materials, a novel approach in all areas of interest was needed. As a result, in a relatively short time, we have made breakthroughs in processing both neat polymer and composites with a new quench match die mold; identified for the first time a reaction of PEEK in the presence of copper metal [15]; and finally, in evaluating PEEK's resistance to solvents, identified its high affinity for methylene chloride and similar other solvents. Collectively, these findings coupled with mechanical testing and characterization not only are opening new ways for processing and utilizing PEEK as a matrix for high performance composites, but also may help in broadening our basic understanding of crystalline polymers in general.



Glass transition temperature $T_g = 144^{\circ}\text{C}$
Crystal melting point $T_m = 334^{\circ}\text{C}$

Figure 1. The chemical structure of polyetheretherketone (PEEK) with some of its physical property characteristics.

STRUCTURE AND MORPHOLOGICAL CHARACTERIZATIONS

The starting point of morphological characterization of any semicrystalline polymer is the determination of its crystallinity level. The value obtained depends very much on both the experimental technique and modelling of the results. For accuracy in analysis, two methods were investigated, differential scanning calorimetry (DSC) and the density gradient technique (DGT) (15). For analysis of the data, a two-phase approximation of the semicrystalline polymer was used to model the measured bulk density of the polymer, viz.:

$$\rho_m = \rho_c x_{vc} + \rho_n x_{vn} \quad (1)$$

where

ρ_m = measured bulk density of the semicrystalline matrix polymer

ρ_c = extracted density of the crystalline phase

ρ_n = extracted density of the noncrystalline phase

x_{vc} = volume fraction of the crystalline phase

x_{vn} = volume fraction of the noncrystalline phase

with

$$x_{vc} + x_{nc} = 1 \quad (2)$$

Previous x-ray studies of PEEK have determined $\rho_n = 1.2626 \text{ g/cm}^3$ and $\rho_c = 1.4006 \text{ g/cm}^3$ (18).

Combining equation (1) and (2) the volume fraction crystallinity may be obtained as a function of the measured and phase densities, viz.:

$$x_{vc} = \frac{\rho_m - \rho_n}{\rho_c - \rho_n} \quad (3)$$

Based on the laws of mass conservation Equation (3) may be extended to incorporate the presence of a third phase in the system like the fibers in a composite made with a semicrystalline polymer, viz.:

$$x_{vc} = \frac{\rho_b - \rho_r x_{vr} - \rho_n (1 - x_{vr})}{(1 - x_{vr}) (\rho_c - \rho_n)} \quad (4)$$

where

ρ_b = measured bulk density of the complete composite system

ρ_r = density of the added reinforcing phase

x_{vr} = volume fraction of the reinforcing phase

x_{vm} = volume fraction of the matrix (crystal and noncrystal)

with

$$x_{vm} + x_{vr} = 1 \quad (5)$$

As expected, if x_{vr} is set equal to zero as in the case of neat polymer matrix, then Equation 4 reduces to Equation 3. If x_{vr} is set equal to 1, then it can easily be seen that x_{vc} becomes identically zero since the reinforced density become the measured density. On a similar basis assuming volume additivity of the components in the composite the mass fraction crystallinities for both neat resin and the composite may be easily calculated, viz.,

$$x_{mc} = \frac{\rho_c}{\rho_m} x_{vc} \quad (6)$$

and for the composite

$$x_{mc} = \frac{\rho_c \rho_r \rho_b (1 - x_{mr}) - \rho_n \rho_c (\rho_r - \rho_b x_{mr})}{\rho_r \rho_b (1 - x_{mr}) (\rho_c - \rho_n)} \quad (7)$$

where

x_{mc} and x_{mr} are the mass fractions of the crystalline phase and the reinforcement defined as

$$x_{mx} + x_{mn} = 1 \quad (8)$$

$$x_{mr} + x_{mm} = 1 \quad (9)$$

These simple but useful expressions allow for calculation of either the volume or mass fraction of crystals present either in the neat matrix form or in the composite. In high performance carbon fiber reinforced composites, the mass fraction of the reinforcement (x_{mr}) is easily measured by pyrolysis of the matrix at high temperatures and measurement of the residual weight of the fibers. Thus, if the bulk density of the composite ρ_b is also measured in a density gradient column, then with the known values of ρ_c and ρ_n as well as those for carbon fiber ($\rho_r = 1.8$), the mass fraction crystallinity of the matrix polymer x_{mc} can be calculated from equation (7).

In addition to calculating the crystallinity of both neat resin and the composite with the density gradient column technique, differential scanning calorimetry (DSC) can also in principle be used. A typical DSC trace of PEEK

measured on a Dupont thermal analysis system is shown in Figure 2. As can be seen for that particular specimen, an additional crystallization peak past the glass transition temperature of the material was observed if the sample examined was not crystallized to its equilibrium point. Further heating produces the final melting of the crystal phase for the sample being examined. This behavior of additional crystallization has been observed with polyethylene terephthalate but to our knowledge it was the first time that it has been observed for PEEK. However, because of this phenomena calculation of crystallinity by DSC is not as direct as with the density gradient technique. For the pure polymer, if it is assumed that the heat capacity of the polymer is essentially independent of temperature, then the area under the peaks divided by the sample weight would be proportional to the crystallization process indicated in the thermogram. Accordingly, the mass fraction crystallinity of the polymer examined in a DSC thermogram like the one shown in Figure 2 may be calculated as

$$x_{mc} = \frac{H_M - H_A}{H_F} \quad (10)$$

where

H_M = enthalpy of melting calculated as the area under the crystal melting transition per unit weight of sample.

H_A = area under the additional crystallization transition per unit weight of sample

H_F = theoretical heat of fusion for a pure crystalline phase reported as 130 J/g (20)

If it is further assumed that for a high performance carbon reinforced composite, the carbon fiber reinforcement does not influence the transitions of the polymer being tested in the DSC experiments, then the mass fraction crystallinity of the matrix in a composite can also be calculated as

$$x_{mc} = \frac{H_M - H_A}{(1 - x_{mr}) H_F} \quad (11)$$

where as before x_{mr} is the mass fraction of the reinforcement. As will be shown later in this work, the equivalence for Equations 6 with 10 and 7 with 11 for calculating the mass fraction crystallinity in the neat polymer and in

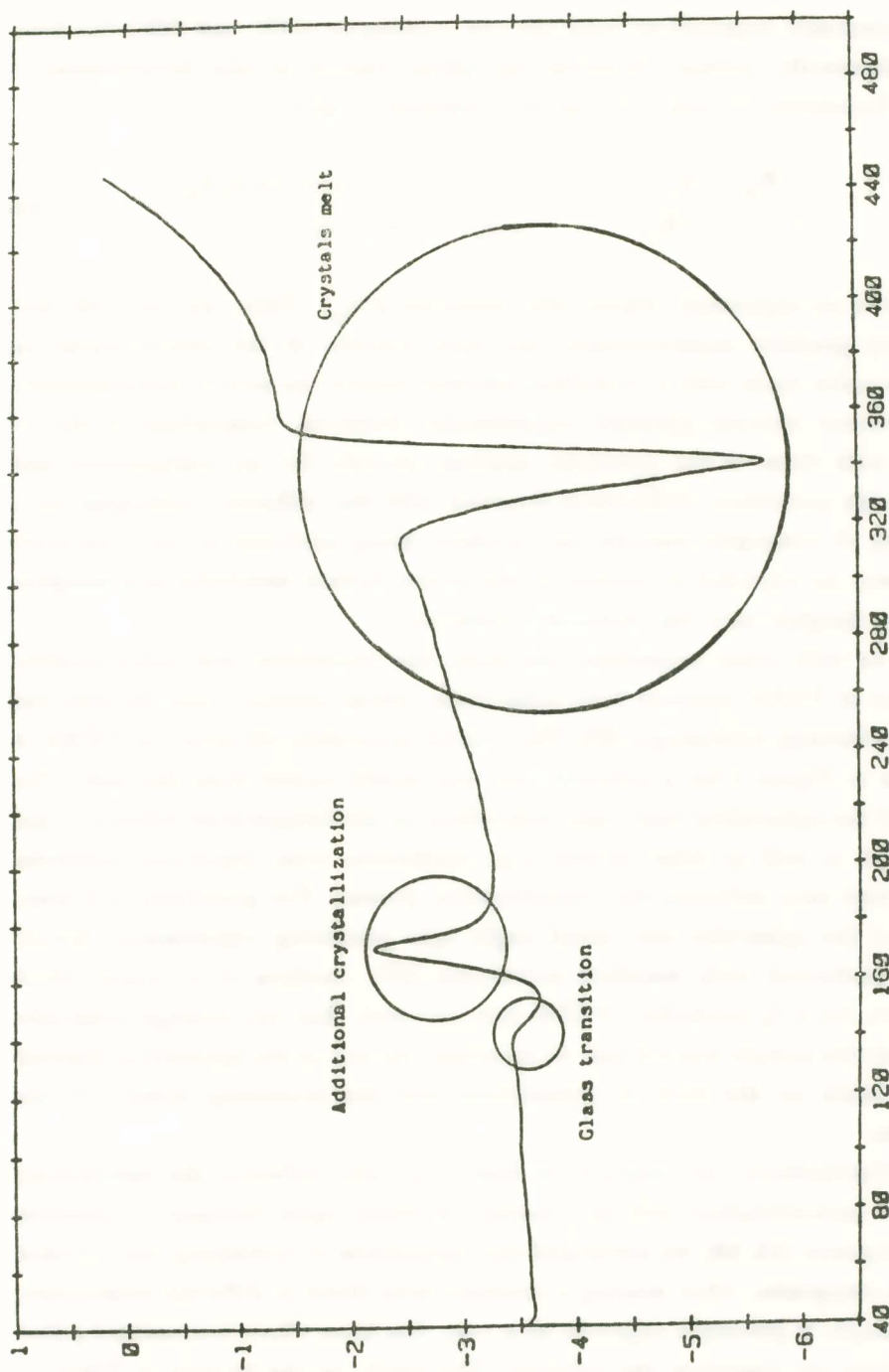


Figure 2. Typical Differential Scanning Calorimetry (DSC) trace for PEEK sample showing its glass transition temperature, additional crystallization exotherm and melting endotherm. Experiment was performed on 9.2 mg sample and at heating rate of 16°C/min.

the composite respectively with the two techniques (DGC and DSC) has been experimentally proven. However, an added feature of this development is that Equations (7) and (11) can be combined to give:

$$\frac{H_M - H_A}{(1 - x_{mr}) H_F} = \frac{\rho_c \rho_r \rho_b (1 - x_{mr}) - \rho_n \rho_c (\rho_r \rho_b x_{mr})}{\rho_r \rho_b (1 - x_{mr}) (\rho_c - \rho_n)} \quad (12)$$

which is an expression whose only unknown is x_{mr} . Thus, by the DSC and density gradient measurements, the mass fraction of the reinforcement in a composite made with a crystalline polymer matrix can now be independently determined without pyrolytic experiments. However, comparison of the results with those of the pyrolysis analysis provide for an independent and verifiable procedure. Differences observed with the different techniques for a variety of composite samples are currently being analyzed in our laboratory and may be expected to provide in the future further structural and morphological insights into the material's behavior.

As with other crystalline polymers, the crystalline and noncrystalline regions of PEEK polymer form spherulites, whose presence may be observed in a polarizing microscope [17]. The typical spherulitic structure of PEEK is shown in Figure 3 for a polymer that was slowly cooled from the melt. The size of the spherulites may vary depending on the temperature history of the polymer as well as other factors (e.g., nucleation sites, impurities, solvents, etc.) that may influence the crystallization process. For quantitative evaluation of the spherulite size, small angle light scattering experiments (SALS) were performed with standard techniques [17]. Analysis of a typical SALS pattern for 9 % crystalline PEEK film provided that the average spherulite size for this sample was 5.2 μm . As expected, the size of the spherulites depends very much on the level of crystallinity and the processing history of the sample.

Furthermore, the presence of fibers may also influence the morphology of the semicrystalline polymer matrix. Building upon findings of previous investigators [13, 19] we developed the capabilities of examining the polymer in the composite. After making a laminate with fibers in different orientation, the sample is grounded edgewise to a very fine layer where transmitted polarized light can penetrate the polymer. The result, as can be seen in Figure 4, is the observation of the spherulitic morphology of the polymer matrix. Cur-

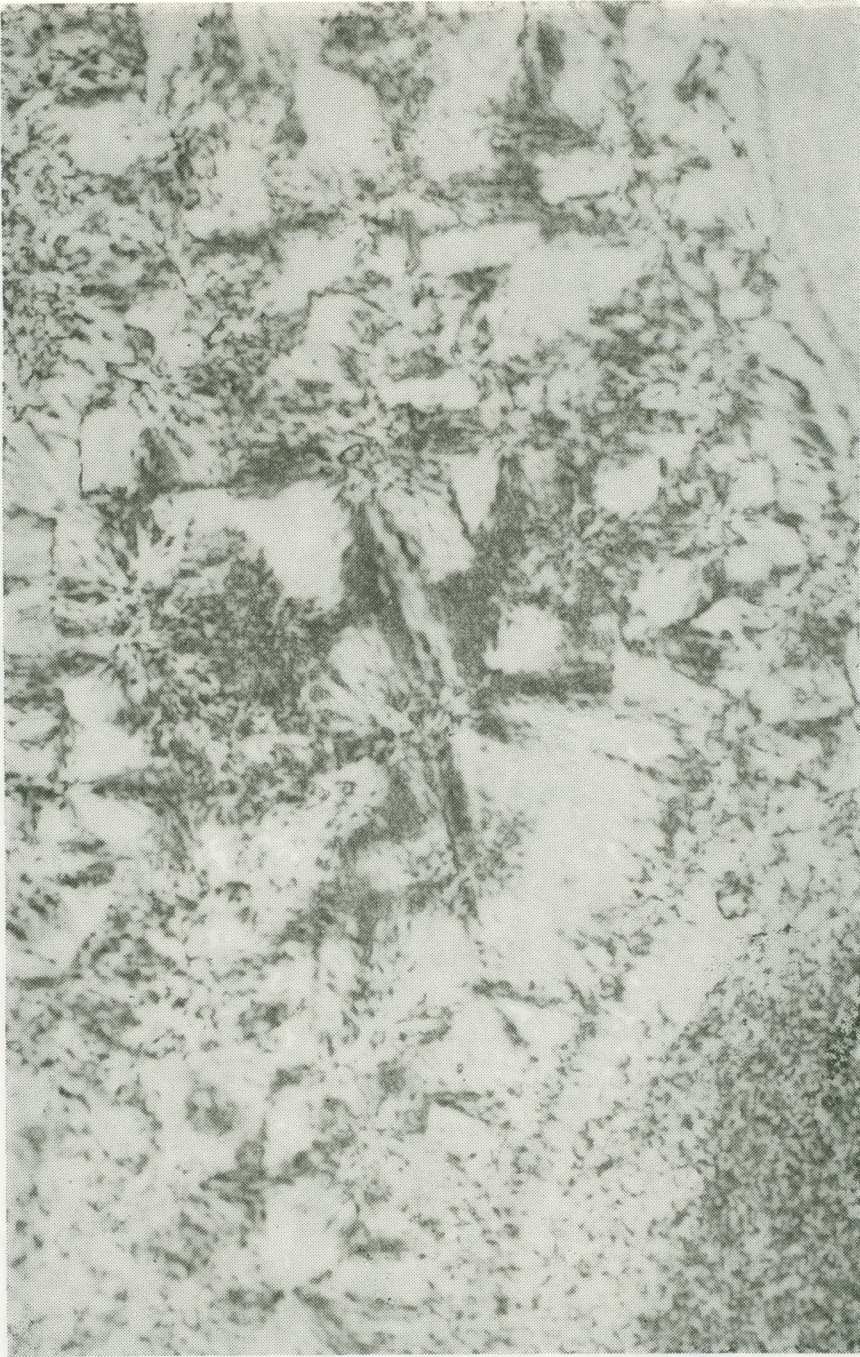


Figure 3. Polarized microscopy photograph of PEEK spherulites.

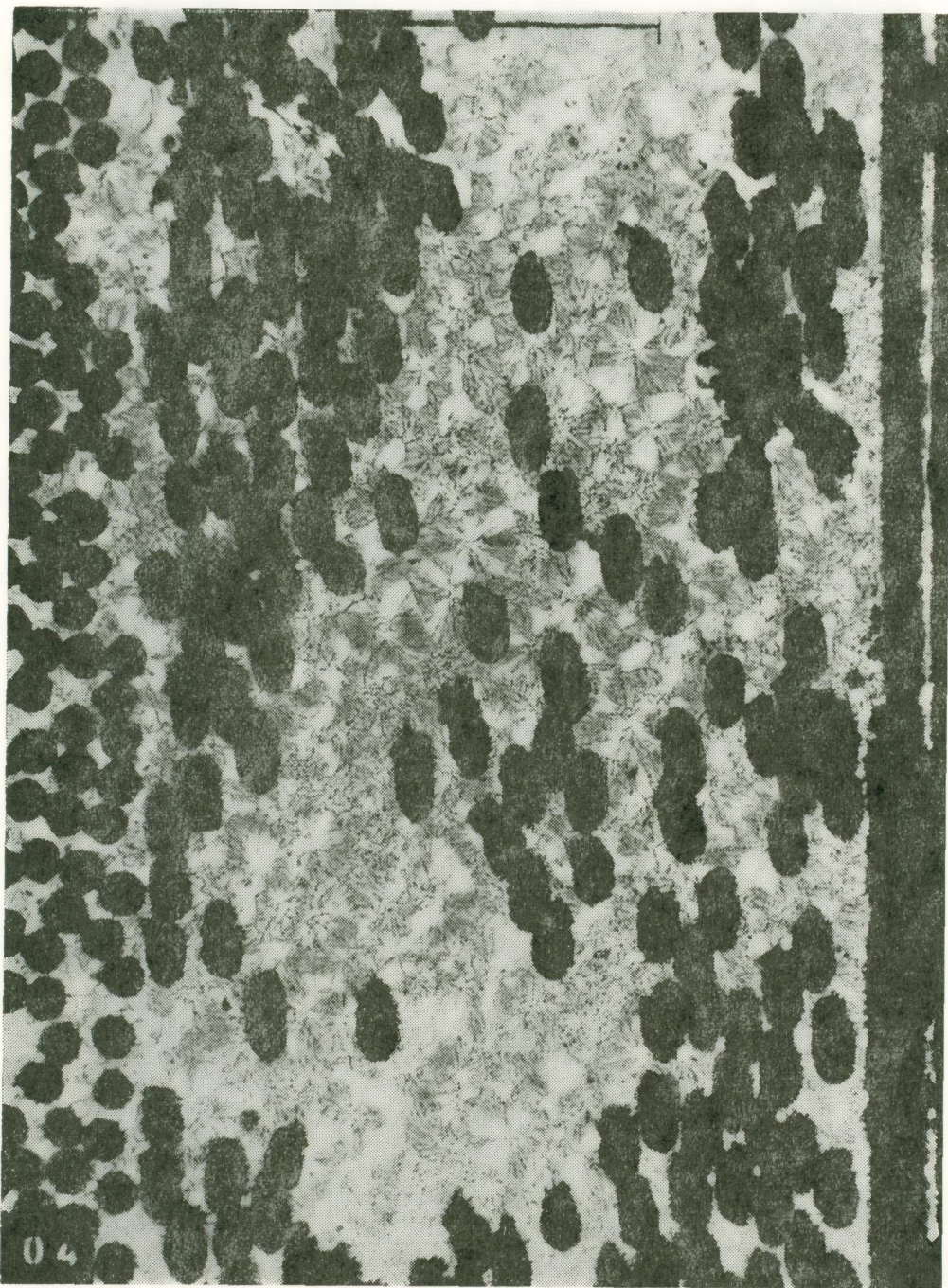


Figure 4. Photograph of edge ground section of PEEK/carbon fiber composite laminate, viewed in the polarizing microscope. Fibers at 0° , 45° , and 90° are shown as parallel rods, oval and round circles respectively. Matrix PEEK polymer shows spherulitic pattern.

rently, several studies are underway in perfecting this technique and to ensure that the grinding process does not alter the polymer's original morphology. In summary, however, for proper evaluation of morphological and property characteristics of composites with crystalline polymer matrices, the processing and sample preparation must be closely monitored and controlled. Accordingly, the major effort in processing development was undertaken as an integral part of this fundamental investigation.

PROCESSING DEVELOPMENTS

PEEK being a high performance thermoplastic must be processed at high temperature (about 385°C). However, in order to achieve proper balance of crystallinity and morphology, it must be cooled at a controlled rate. Furthermore, it is also desirable to be able to have capabilities to quench the polymer without crystallization taking place so as to investigate the properties of the noncrystalline phase of the polymer. After a thorough study of materials and thermal analysis assuming different coolant for heat transfer, a match die mold was designed to operate at temperature in excess of 450°C and capable of cooling the polymer at specified high rates with a maximum of 50°C/sec [15]. The material chosen for the mold was copper to ensure good heat transfer. The cooling liquid chosen was water coming from the side of the mold and exiting from its ends through copper tubing. Enough ports were designed into the mold to allow for a flow rate of 50 gallons/minute. The schematic design of the mold is shown in Figure 5, while pictures of the mold showing all components and the assembled bottom part of the mold are shown in Figures 6 and 7, respectively. The actual mold performance is shown in Figure 8 which plots the cooling rate obtained on the mold surface (after it was heated to 385°C) as a function of water flow rate. The figure shows two curves depending on the method employed for calculation. The first showing the initial cooling rate was calculated from initial slope of the temperature vs time data. The average cooling rate obtained was obtained as an average of slopes calculated from 385°C (the molding temperature) to just below PEEK'S glass transition temperature at 125°C. As can be seen in Figure 8, a phenomena 140°C/sec initial cooling rate (115°C/sec average) was achieved with a water flow rate approaching 45 gallons/minute.

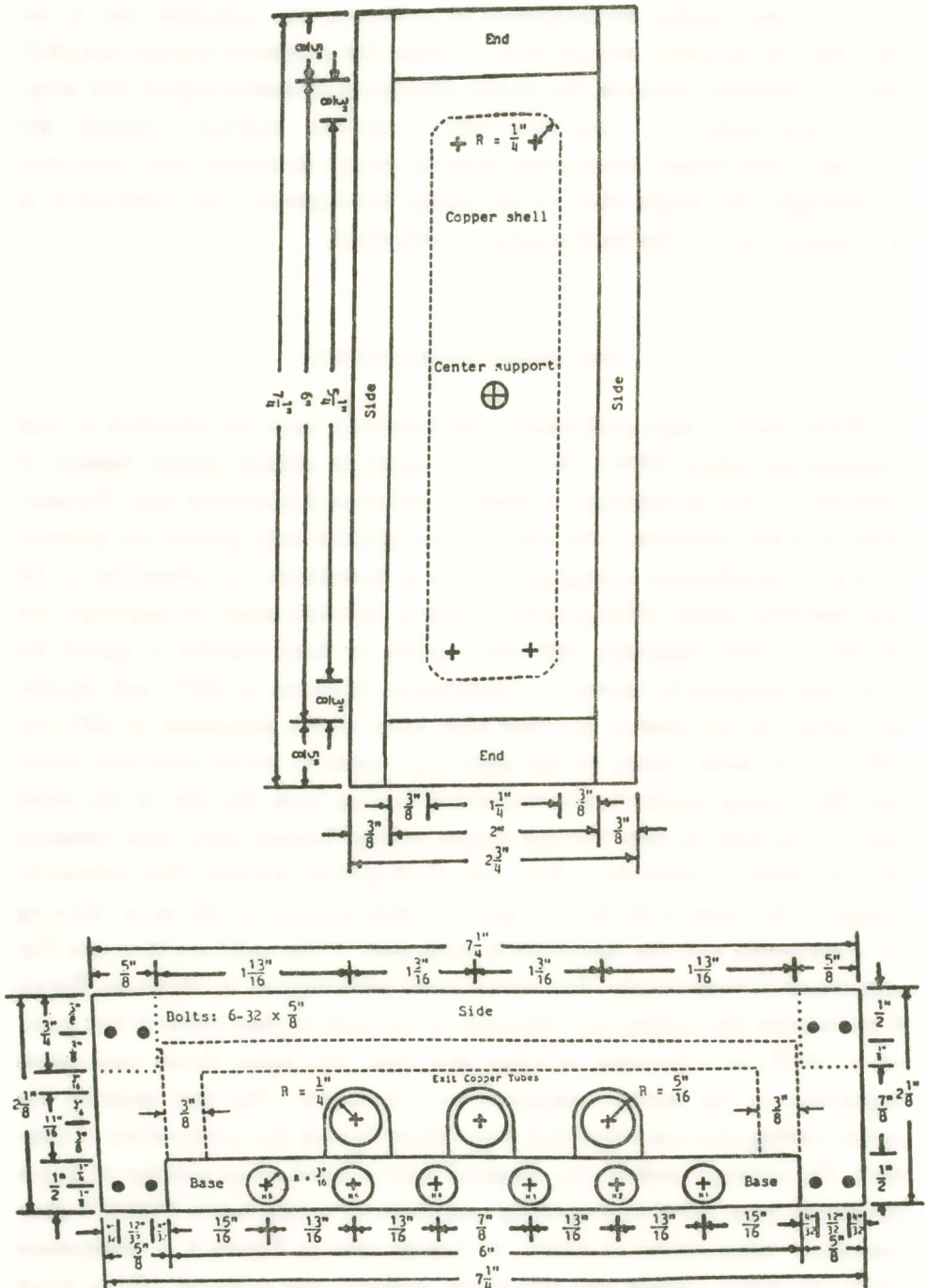


Figure 5. Top and side view of the match die mold. Copper tubes shown are for water used as the coolant. Scale is 0.74:1.

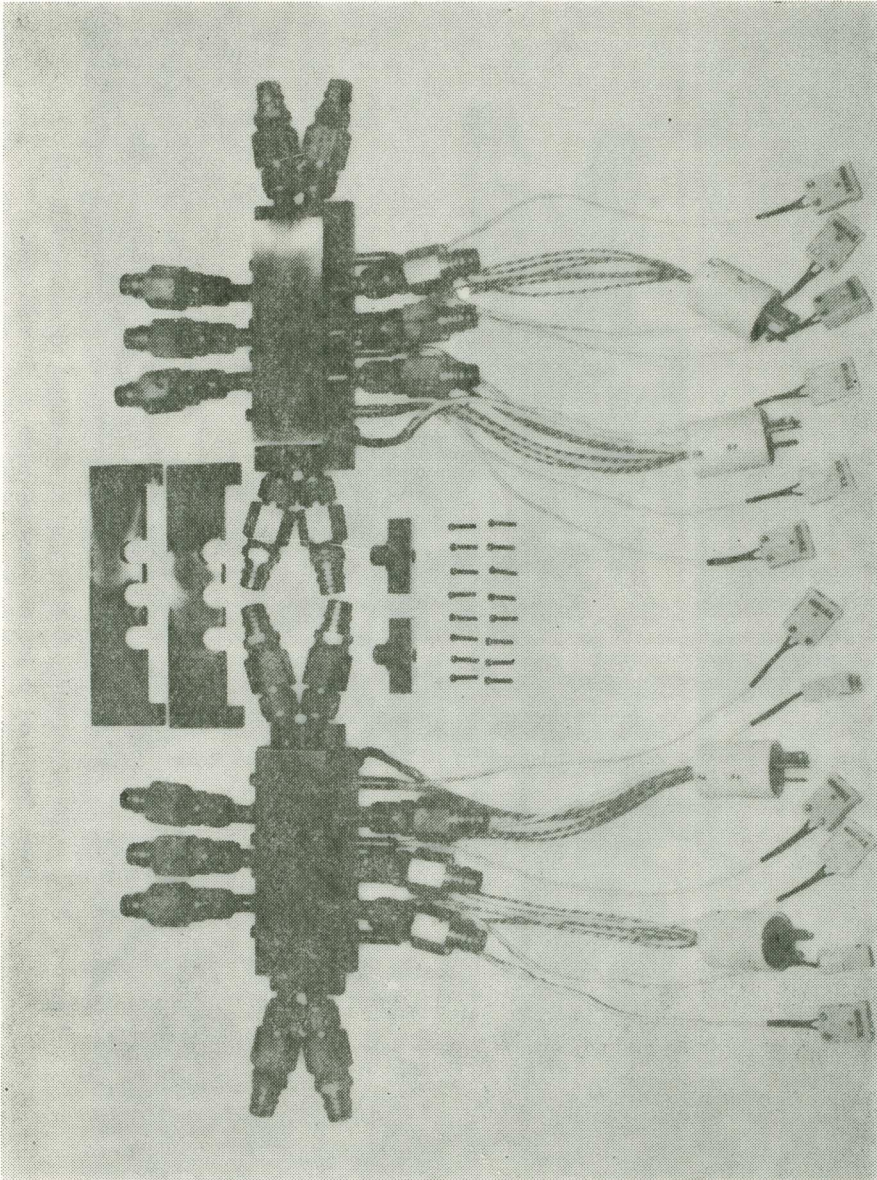


Figure 6. Photograph of the actual match die mold showing all the components, electrical connectors for heaters, and thermocouples and the copper tubes for the water coolant.

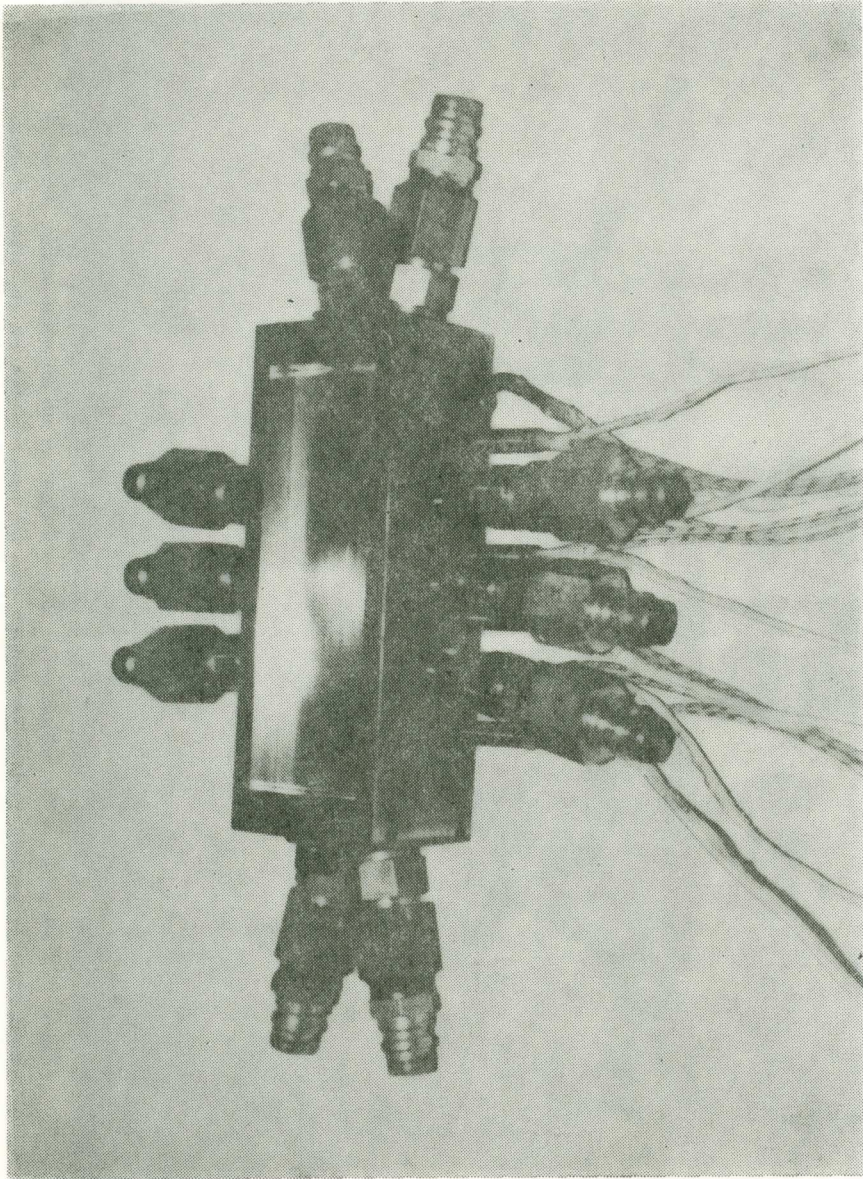


Figure 7. Photograph of assembled bottom part of the match die mold with side plates. Top part is identical except without the side plates.

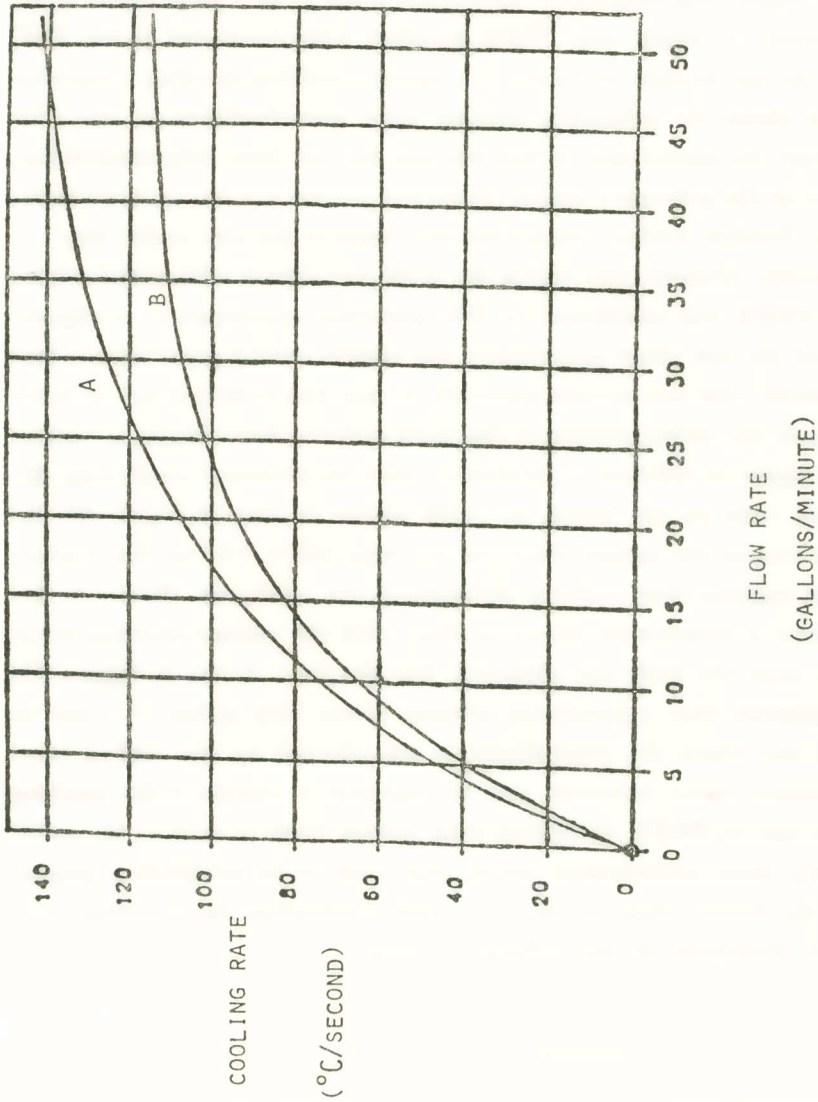


Figure 8. Actual cooling profile performance of the match die mold. Cooling rate at mold surface as a function of water flow rate. A) Initial cooling rate measured at 385°C. B) Average cooling rate from 385°C to 125°C.

Although the cooling capabilities of the developed matched die mold are indeed impressive, the initial samples molded out of the PEEK polymer were full of voids irrespective of the cooling rate employed. After several failed repeated attempts in molding void free samples, a reaction between PEEK and copper was suspected. Conclusive proof of this phenomena came when a mixture of copper and PEEK powders were examined in the DSC experiment. As can be seen in Figure 9, a strong exotherm showing a reaction beginning at about the polymer's melting point was identified for the first time. Although the mechanism of this reaction has not been fully established, a breakdown of the polymer's chains producing phenol is a strong hypothesis at this time. Further studies concerning this reaction are also under way.

To proceed, however, the match die mold was plated with nickel whose inertness to PEEK was established by DSC and other experiments. As expected, the nickel did not affect appreciably the mold's cooling performance, but indeed produced void free sample especially if care was exercised not to have any porosity in the nickel coating of the mold surface. Accordingly, a variety of PEEK samples of different crystallinity could be produced employing different cooling rates on the match die mold as can be seen in Figure 10. As expected, as long as the sample thickness was kept below 0.10 cm the crystallinity of the samples was uniform throughout the thickness. However, for thicker samples a pronounced skin-core effect with the surface showing lower crystallinity than the bulk was observed. For the data shown in Figure 10, it is also apparent that a processing plateau exists from about 1° C/sec to about 30° C/sec where the crystallinity is not affected by the cooling rate. This performance curve, however, may be expected to change if the molding temperature and/or PEEK reinforced with carbon fibers is used in the mold. It is precisely these performance curves that need to be established quantitatively in the future while at the same time evaluating the resulting morphology and properties of the different systems.

PROPERTY EVALUATIONS

Experiments performed for properties to establish the desired correlation with morphology and processing include exposure to different fluid environments, dynamic mechanical characterizations, and typical stress-strain experiments. For fluid and dynamic mechanical characterizations, three basic

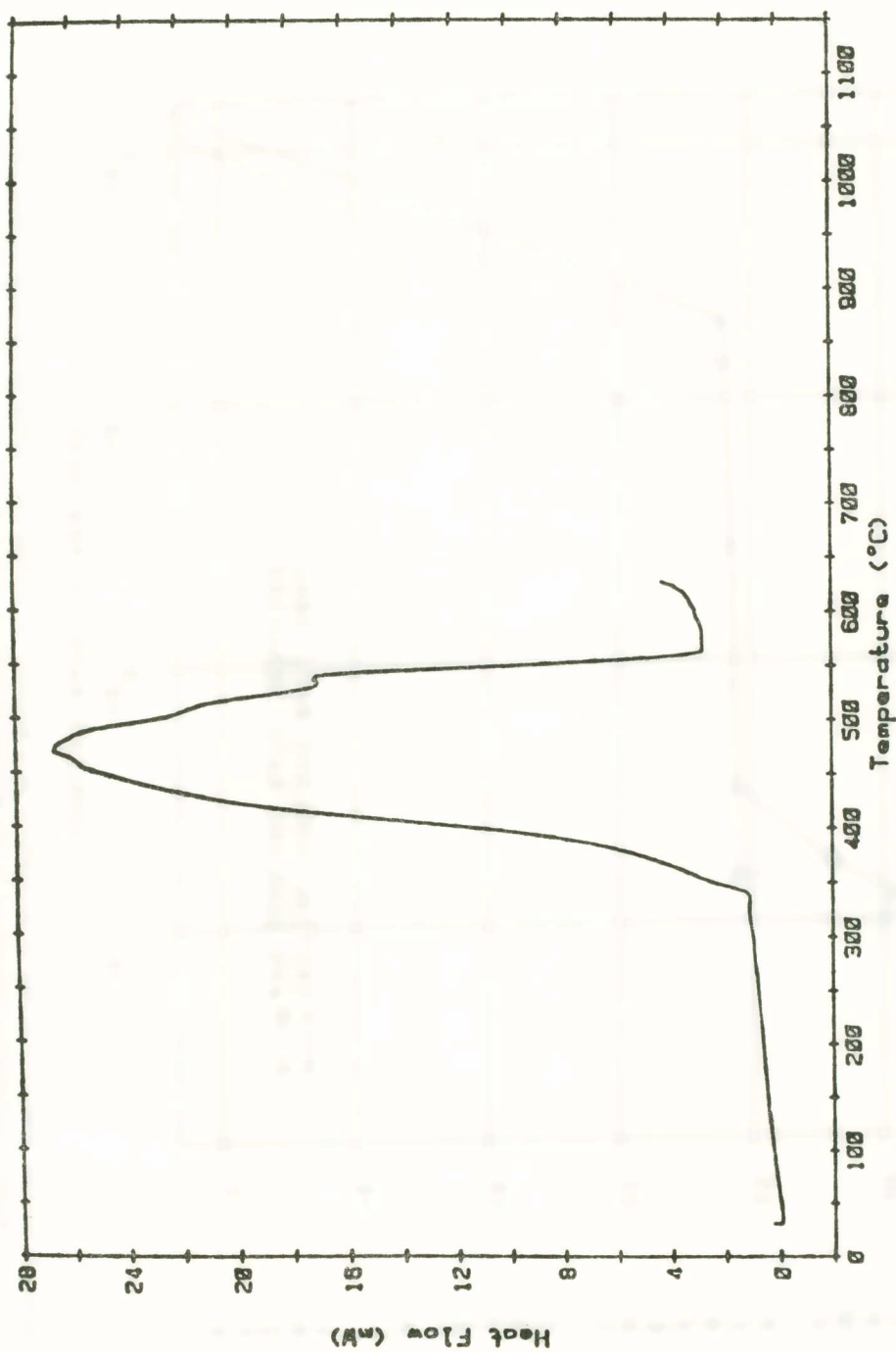


Figure 9. Differential scanning calorimetry trace for PEEK/copper powder sample showing the existence of a highly exothermic reaction with onset temperature at 340°C. Experiment was performed on 12.9 mg sample and heating rate of 1°C/min.

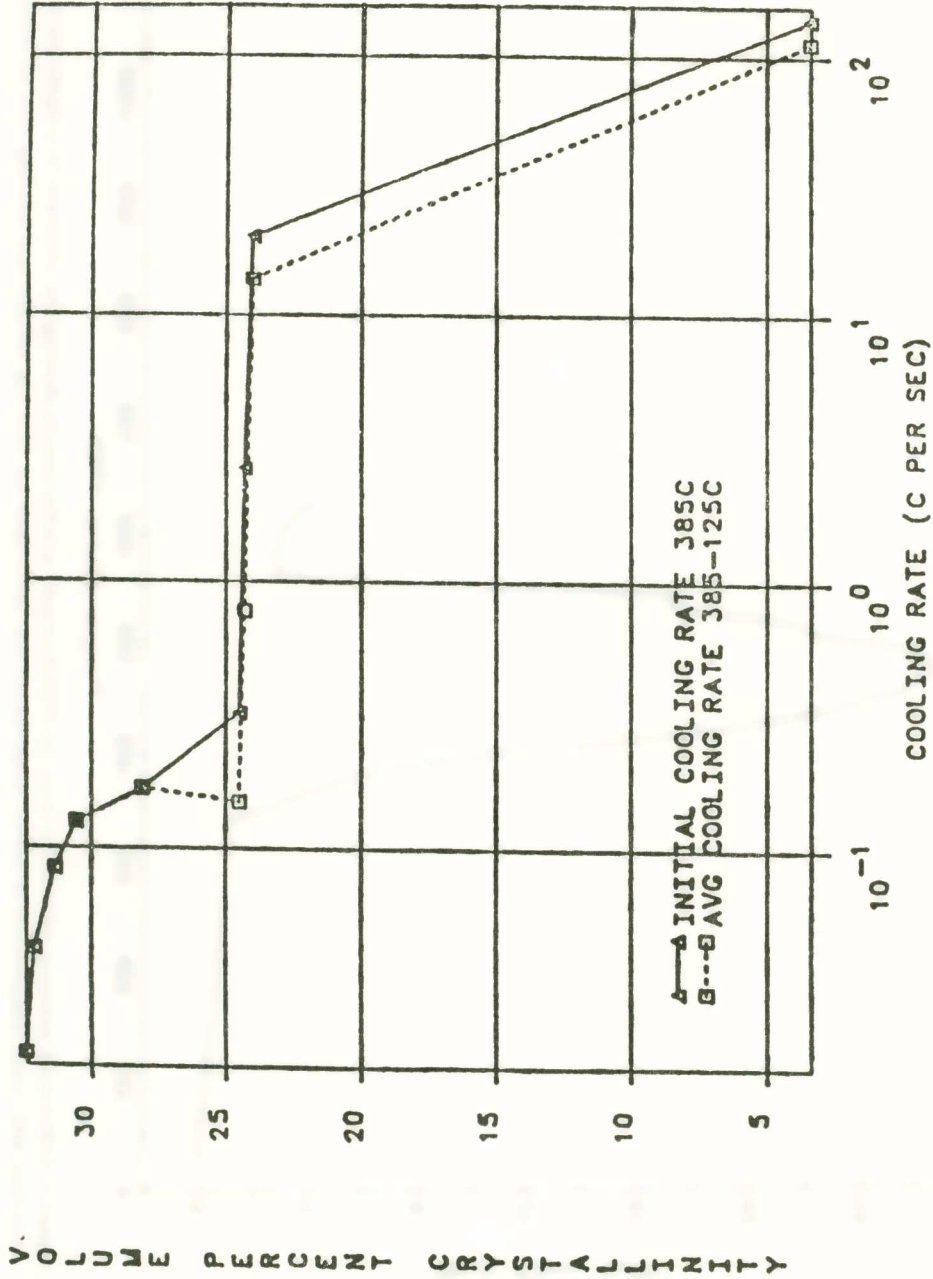


Figure 10. Sample performance plot of crystallinity as a function of cooling rate. Initial and average cooling rates are shown. Crystallinities determined by the different techniques and methods of analysis developed.

samples were examined: a neat PEEK polymer film sample with 9 % crystallinity ($x_{vc} = 0.09$), a neat polymer PEEK sample with 26 % crystallinity ($x_{vc} = 0.26$), and a composite sample made with 60 % unidirectional continuous carbon fibers ($x_{vr} = 0.60$) within a 24.4 % crystalline PEEK matrix ($x_{vc} = 0.24$). For the stress-strain experiments, samples examined had a broader range of crystallinities produced with the quench mold ($x_{vc} = 0.09, 0.19, 0.26, 0.30, 0.33$). All sample crystallinities were determined with the experimental and analytical methods described earlier.

The solvents chosen for the work were methylene chloride, water, and an all-purpose aviation lubricant, Skydrol. This choice was dictated by previous experience with other matrix polymers used in high-performance applications for airplane structures [16].

The primary experiment in fluid exposure was to record the sample's weight gain as a function of time immersed in the different fluids. These experiments, summarized in Figure 11, led us to observe for the first time the affinity of PEEK to absorb large amounts of methylene chloride. However, the same experiments confirmed the excellent resistance of PEEK in water and Skydrol which are fluids with a high degree of affinity for other polymer matrices such as epoxies and polysulfones, respectively. Furthermore, as can be seen from Figure 11, for the 9 % crystalline PEEK sample, when reached an apparent equilibrium, a 20 % weight gain was observed. However, for the 26 % crystalline PEEK, only a 15 % weight gain of methylene chloride was observed when its apparent weight gain was observed.

These results further suggested that increases in crystallinity decrease the methylene chloride absorption of the material. Furthermore, upon desorption of methylene chloride and measurement of the sample density, additional crystallization in the sample after exposure to the fluid was observed. This additional crystallization measured and calculated with the DGC technique and cross-correlated to DSC experiments was also found to be a function of the starting sample crystallinity and temperature of exposure. Calculation of the crystallinities for the two samples examined is provided in Table I below.

From these results, it can be seen that the crystallinity increases the most for the sample with the lowest starting crystallinity. To further confirm the additional crystallization, polarizing optical photographs of the 9 % crystalline PEEK films were obtained before and after exposure to methylene chloride. As it was explained earlier, with the developed technique, the films

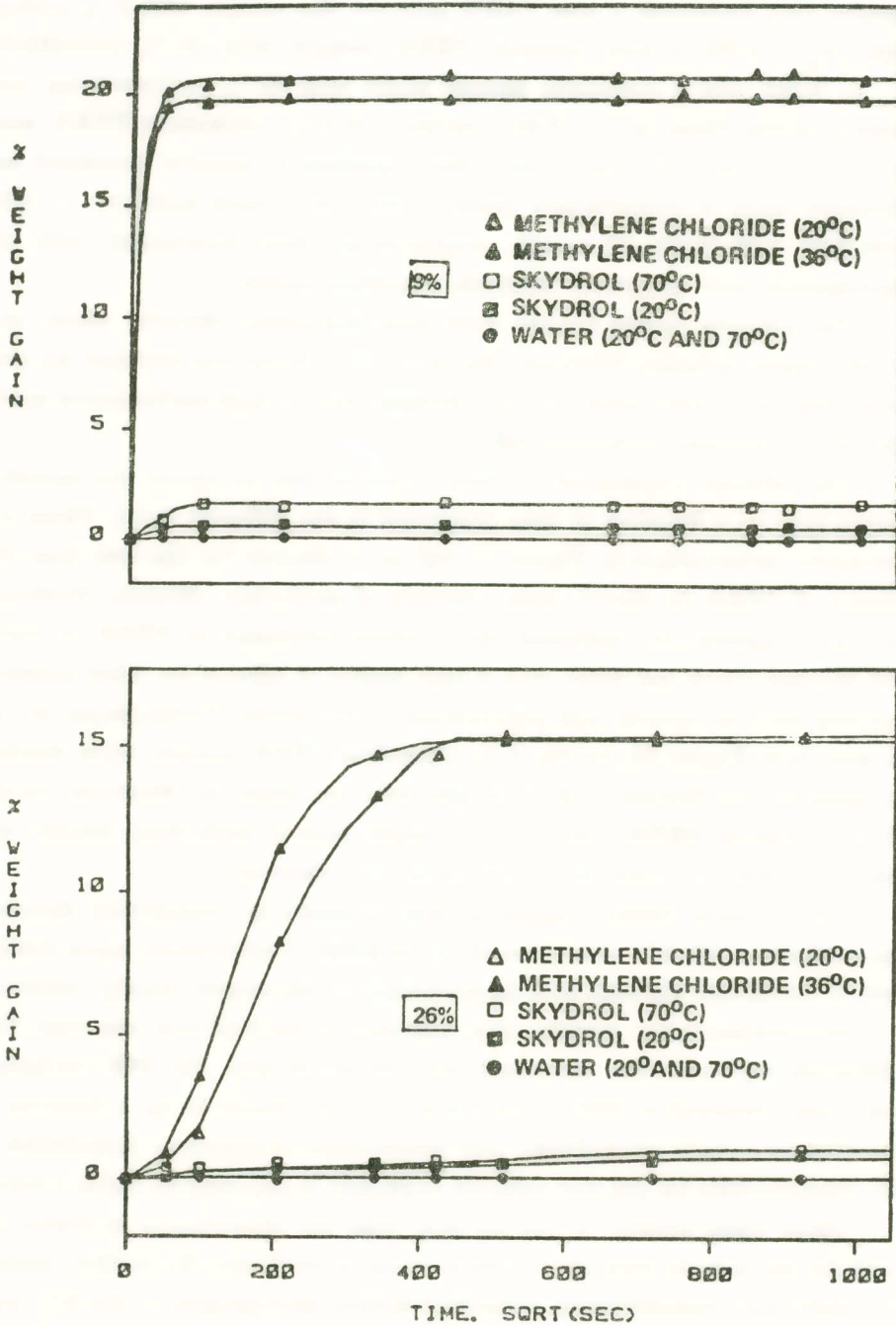


Figure 11. Sorption recorded as weight gain as a function of time for 9% and 26% crystalline PEEK film samples exposed to different fluid environments and temperatures.

TABLE I
*Volume present crystallinities of PEEK samples before
 and after exposure to methylene chloride*

CONDITION	x_{vc}	$\times 100$
Initial crystallinity	9 %	26 %
After exposure to methylene chloride at 20°C	21	34
After exposure to methylene chloride at 36°C	33	37

were grounded on their edges so, in effect, the photographs show the polymer through the thickness. As expected, the 9 % crystalline PEEK film before exposure to methylene chloride shows numerous but small spherulites as can be seen in Figure 12. However, after sorption and desorption of this sample to methylene chloride, the evidence of additional crystallization through the thickness is evident although the spherulitic pattern is no longer there, as shown by the lines from both top and bottom edges of the film leading to its center. It is apparent from the photographs of Figure 12 that a different morphology has been produced after the polymer was exposed to methylene chloride. The influence of this morphology on the material properties is actively being investigated. To demonstrate that the sorption phenomena could easily be accounted for in terms of neat polymer results, it will be instructive at this point to examine also the composite results. Figure 13 shows that the sorption of methylene chloride in the PEEK/carbon fiber composite closely parallels the neat polymer sorption data of the 26 % crystalline neat polymer PEEK film. Indeed, if the presence of 60 % by volume of the carbon fibers is accounted for, which provides for a reduced amount of PEEK polymer available for methylene chloride sorption, the calculated weight gain per gram of polymer is 17 % for 20°C and 16 % at 36°C. These levels correspond very well with the level of crystallinity of 24% for the PEEK polymer in the composite. Thus, the data provide support that the crystallization process is also happening in the composite as well, while the process should not be very different than the neat polymer results. Polarizing photographs of the composite samples have confirmed this hypothesis.

Finally, to provide a measure of the mechanical material behavior as well as additional information concerning the polymer's supramolecular structure, dynamic mechanical measurements were performed on the samples with the two distinct crystallinities. The data shown in Figure 14 in terms of the

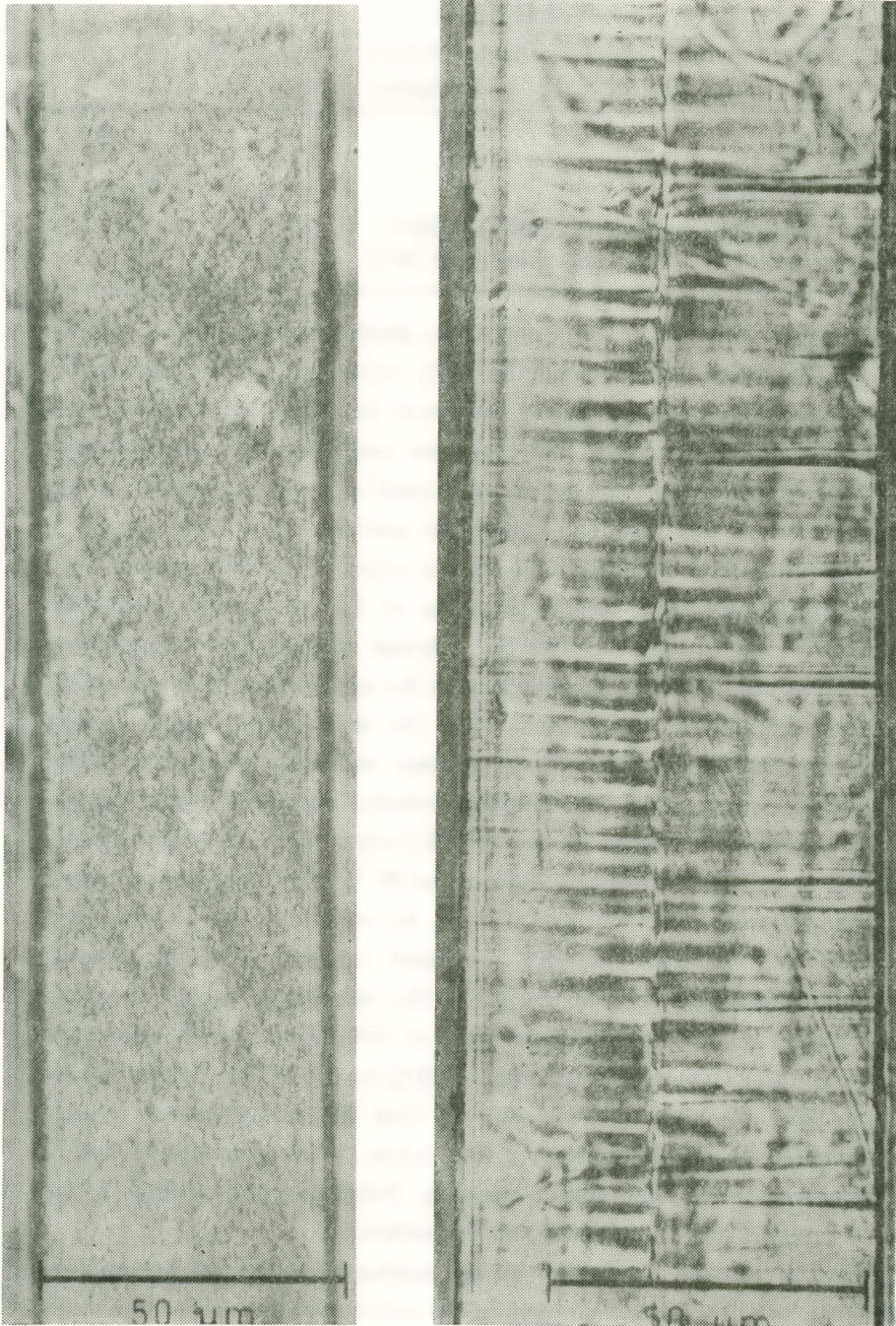


Figure 12. Photographs of edge ground section of the 9% crystalline PEEK film in the polarizing microscope. A) sample showing spherulitic structure before exposure to methylene chloride. B) sample showing additional crystallization after sorption and desorption of methylene chloride.

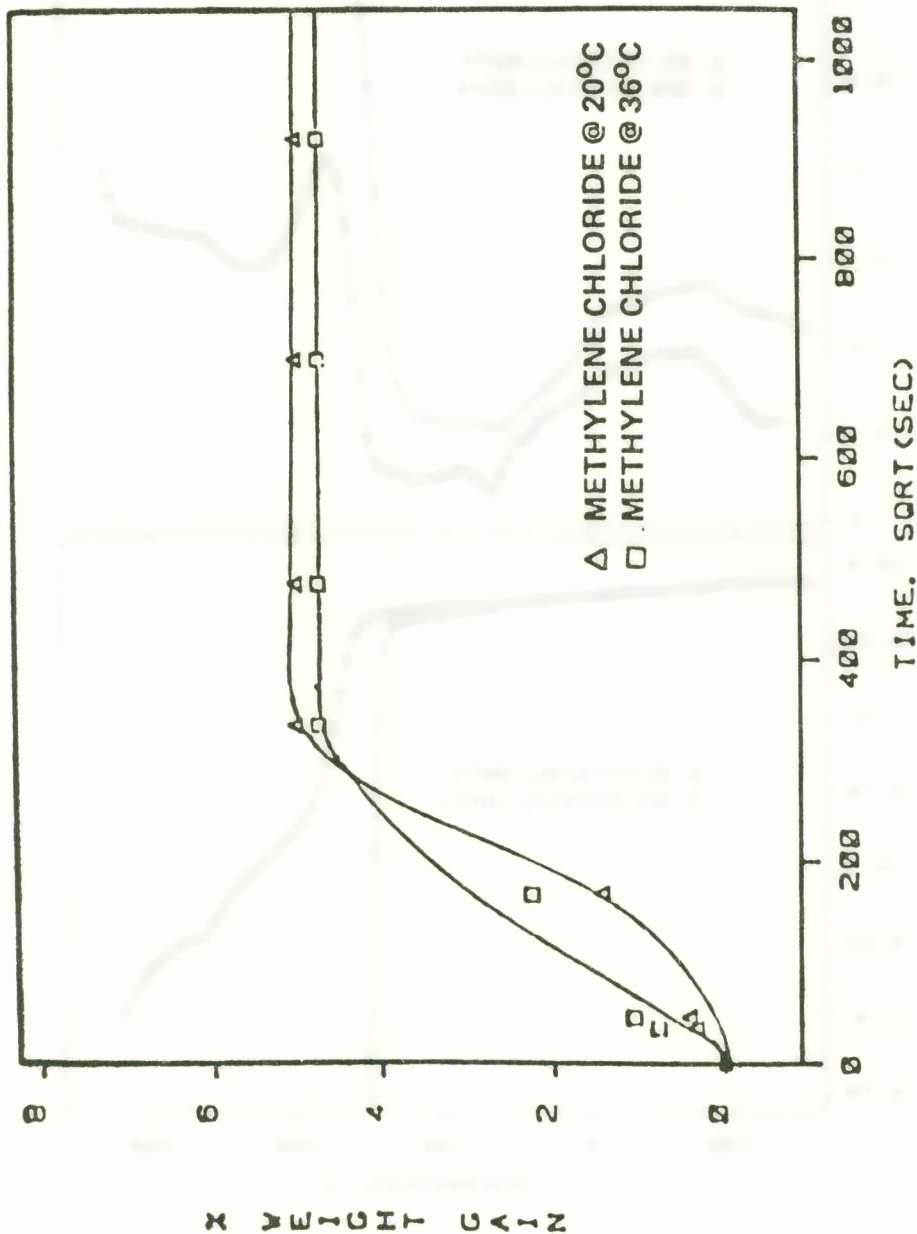


Figure 13. Sorption recorded as weight gain as a function of time for PEEK/60% carbon fiber unidirectional composite exposed to methylene chloride at two different temperatures.

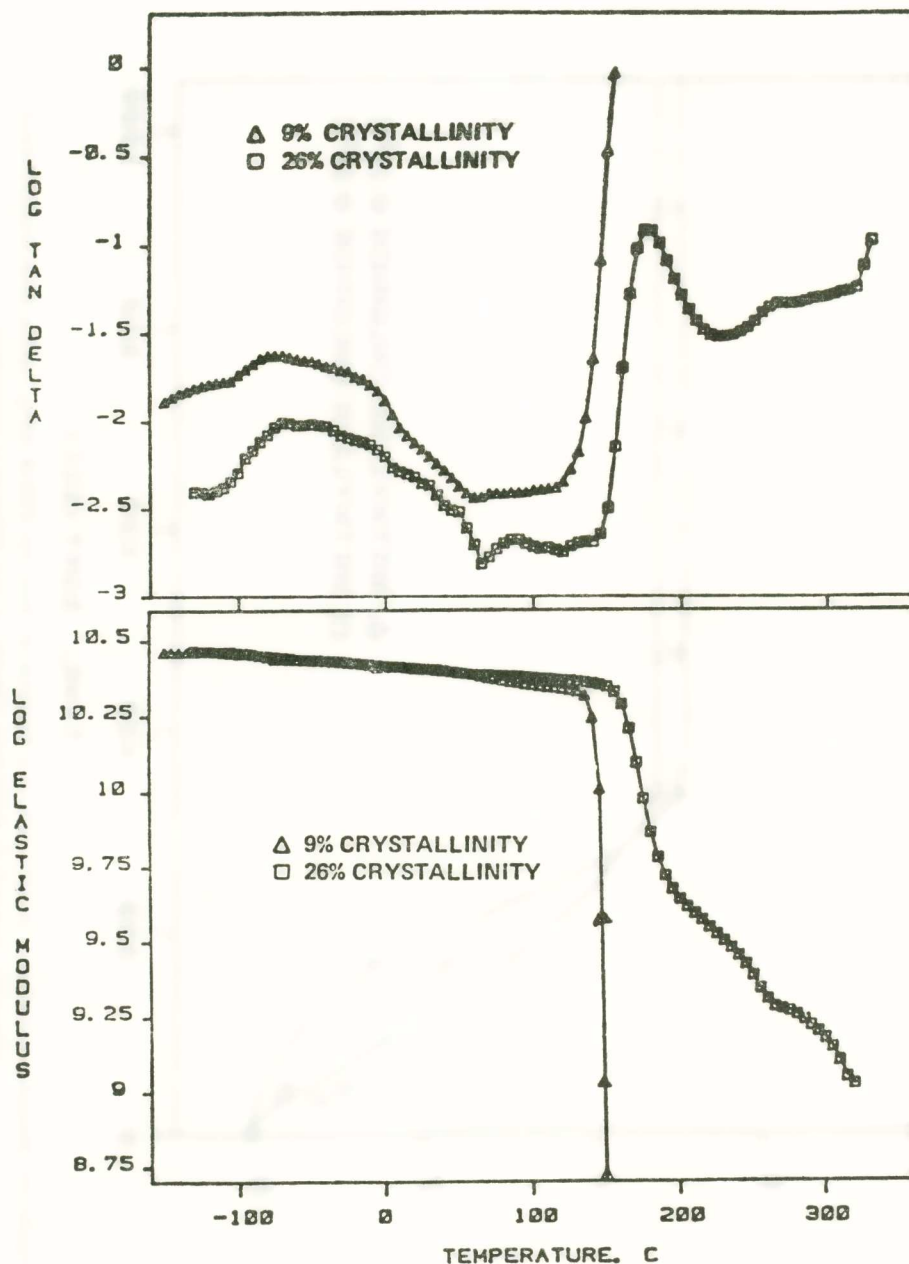


Figure 14. Dynamic mechanical properties of PEEK measured in tension at 11Hz frequency and a heating rate of 1°C/minute. A) Tan δ as a function of temperature. B) Elastic modulus as a function of temperature.

elastic modulus and $\tan \delta$ demonstrate in general that the PEEK polymer exhibits two basic viscoelastic transitions. There is a broad transition which occurs at approximately -60°C (β transition) and the material's glass transition around 140°C (α transition). As expected, it is the α transition which appears to have the greatest influence on the material's modulus and thus on the crystallinity as well. As expected with other crystalline polymers as well, the increase in crystallinity is reflected in the $\tan \delta$ transitions being shifted to higher temperatures and becoming lower in magnitude. The 9 % crystalline sample became very soft at the onset of the α glass transition and the modulus decreased catastrophically ending the experiment. However, the data obtained with the 26 % crystalline sample showed increased stiffness passed the α transition and up to the crystal melting point.

To place in perspective the effect crystallinity in conjunction with the crystallization phenomena of PEEK in the presence of methylene chloride, the dynamic mechanical data of a 9 % crystalline sample that has absorbed in methylene chloride were measured and compared to a 9 % crystalline sample that had absorbed and desorbed methylene chloride. In plotting the results of these experiments, the dynamic data of the 26 % crystalline PEEK sample with no exposure to methylene chloride provided earlier are also plotted for comparison in Figure 15 since this sample is quite close in crystallinity to the methylene chloride treated 9 % crystalline samples. Therefore, the differences between the samples are the presence or absence of methylene chloride and the different morphologies and crystallinities caused by the fluid exposure. As can be seen from the data of Figure 15, the presence of methylene chloride in PEEK shifts the $\tan \delta$ transition to higher temperatures while increasing the magnitude of the transitions. The higher baseline below the glass transition indicates that methylene chloride has a plasticization effect, even after crystallization, that lasts until the sample's glass transition. Because the boiling of methylene chloride is 40°C while the data indicates that this plasticization effect continues up to 140°C , it can easily be hypothesized that during the crystallization process in methylene chloride the noncrystallized regions of the polymer also retain a quantity of the solvent which is released only at the glass transition. Indeed, this phenomenon has also been confirmed by thermal expansion measurements on these samples. The sorbed methylene chloride in the sample is responsible for lowering the modulus of PEEK but, upon desorption, the

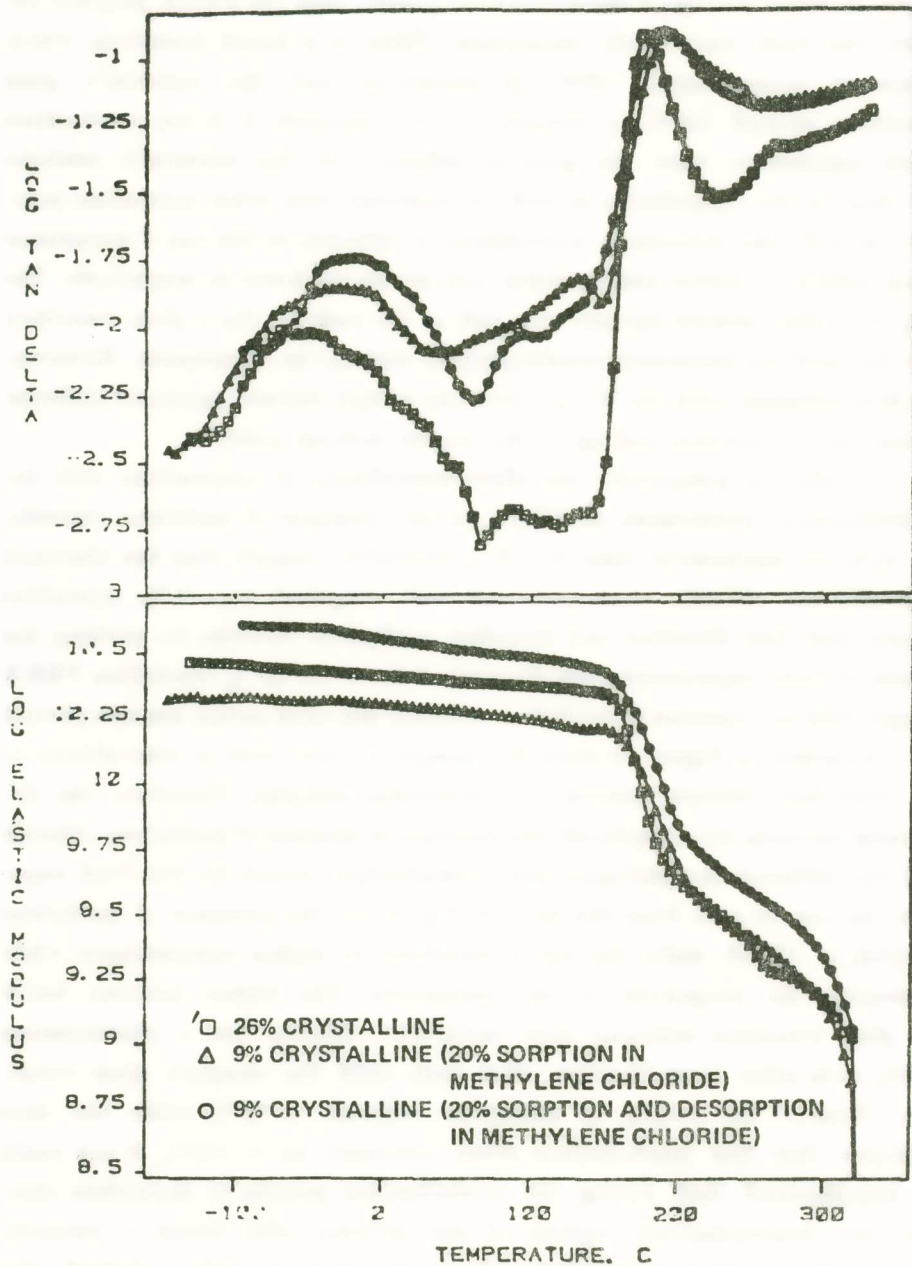


Figure 15. Dynamic mechanical properties of 9% crystalline PEEK samples after sorption and desorption in methylene chloride. The data for a 26% crystallized PEEK sample without exposure to methylene chloride is also plotted for comparison. All data measured in tension at 11Hz frequency and 1°C/minute heating rate. A) Tan δ as a function of temperature. B) Modulus as a function of temperature.

crystallinity is really the determining factor in the sample's modulus. As the data had shown, the sample exposed at 36°C to methylene chloride after desorption had a crystallinity of 33 % and thus its modulus plotted in Figure 15 is higher than the 26 % crystalline sample plotted for comparison. Thus, these simple, but important, experiments elucidate the role of methylene chloride as it may influence the mechanical performance of PEEK both as a plasticizer and as a solvent inducing crystallization. Finally, typical room temperature stress-strain experiments were performed on the neat PEEK polymer samples, made with the quench die mold, and the results are shown in Figure 16. As can be seen, increases in crystallinity lead to increases in both the modulus and strength as shown also in Figure 17 and 18, respectively. However, as expected, increases in crystallinity lead to a general decrease in the strain to failure as can be seen with the data also plotted in Figure 18. If it is assumed that to a first approximation, the toughness of the polymer is related to the area under its exhibited stress-strain curve, PEEK'S toughness is observed to decrease with increasing crystallinity according to our data. However, caution should be exercised before any generalizations are made between toughness and crystallinity. First, with crystalline polymers, it is well established that they may exhibit totally different mechanical properties (including modulus, strength, toughness, etc.) even if their level of crystallinity is kept constant. This is because other morphological features on the polymer may play an important role in determining mechanical properties. Specifically, however, the mechanical data of Figure 16, when examined in conjunction with the crystallinity performance curve of Figure 10, suggest that for normal processing conditions capable of cooling the polymer between 0.1°C/sec and 30°C/sec, no significant changes in crystallinity and resulting mechanical properties should be expected. However, this phenomenon may be drastically altered with different processing conditions and/or reinforcements present, giving rise to distinct morphologies and resulting mechanical properties. Accordingly, these effects need to be completely evaluated and understood if the full potential of these new composite systems is to be realized in the near future.

CONCLUSION

This work has covered significant findings to date while we have been investigating the processing, structure and properties of polyetheretherketone

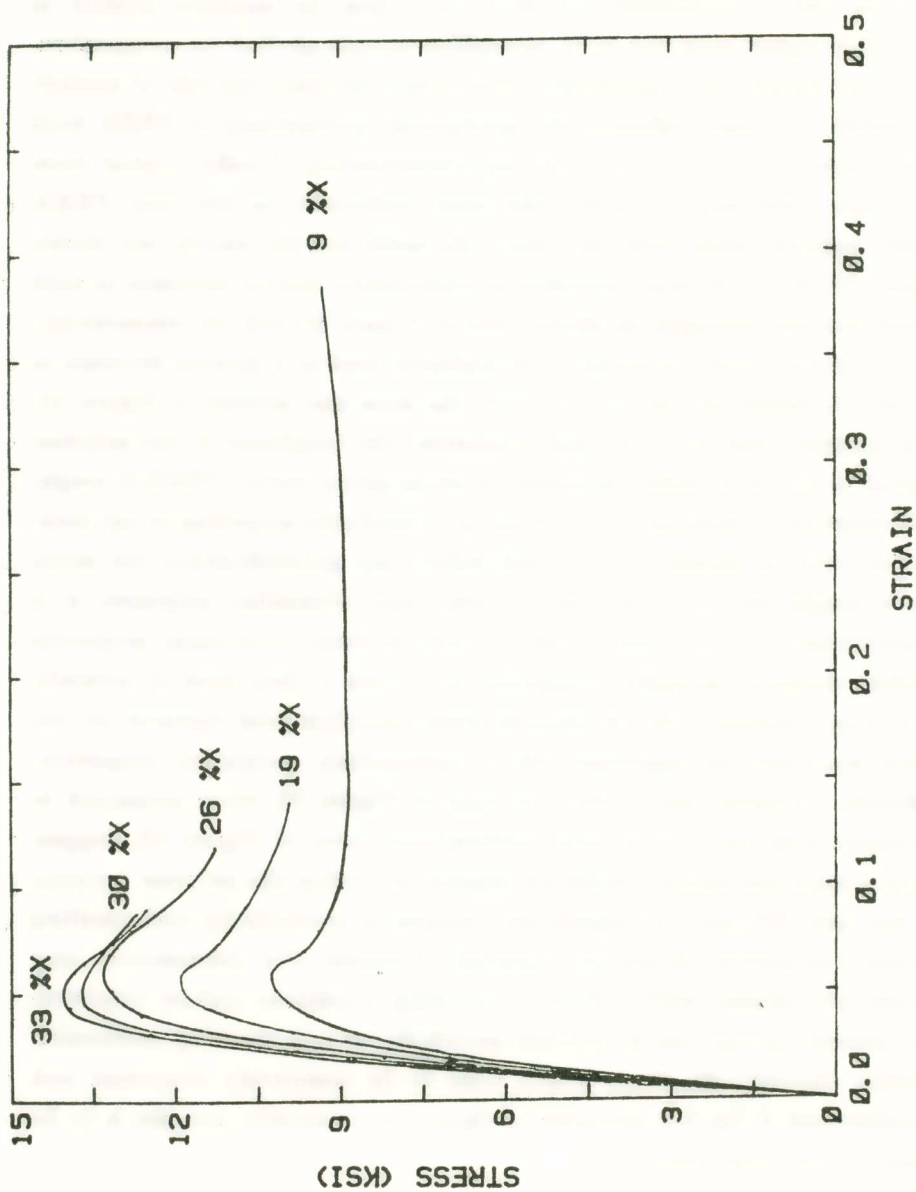


Figure 16. Tensile stress-strain curves for neat PEEK samples of different percent crystallinities shown on the curves ($v_x \times 100$) made at room temperature and strain rate of 0.045 min^{-1} .

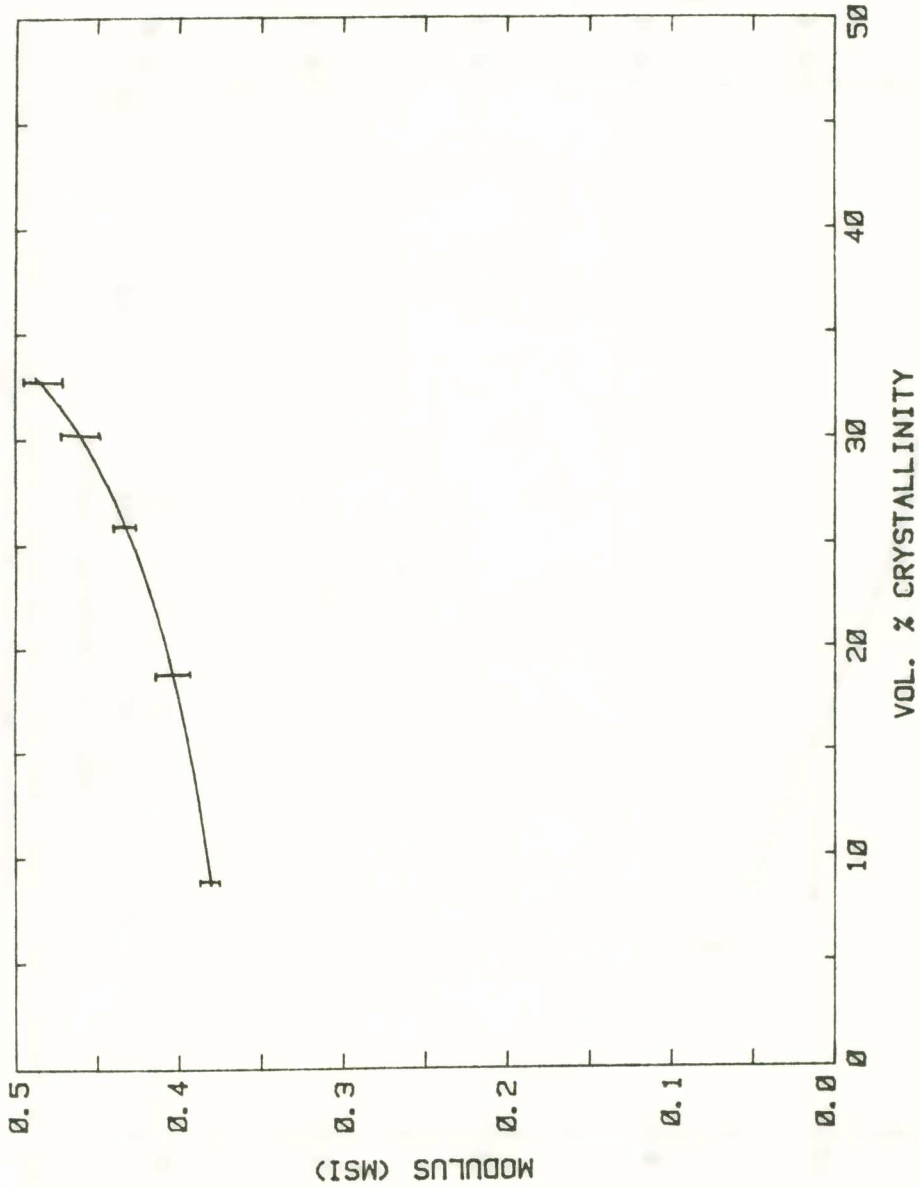


Figure 17. Modulus values in MSI ($\text{PSI} \times 10^6$) of PEEK samples with different crystallinities calculated from the initial slope values of Figure 16.

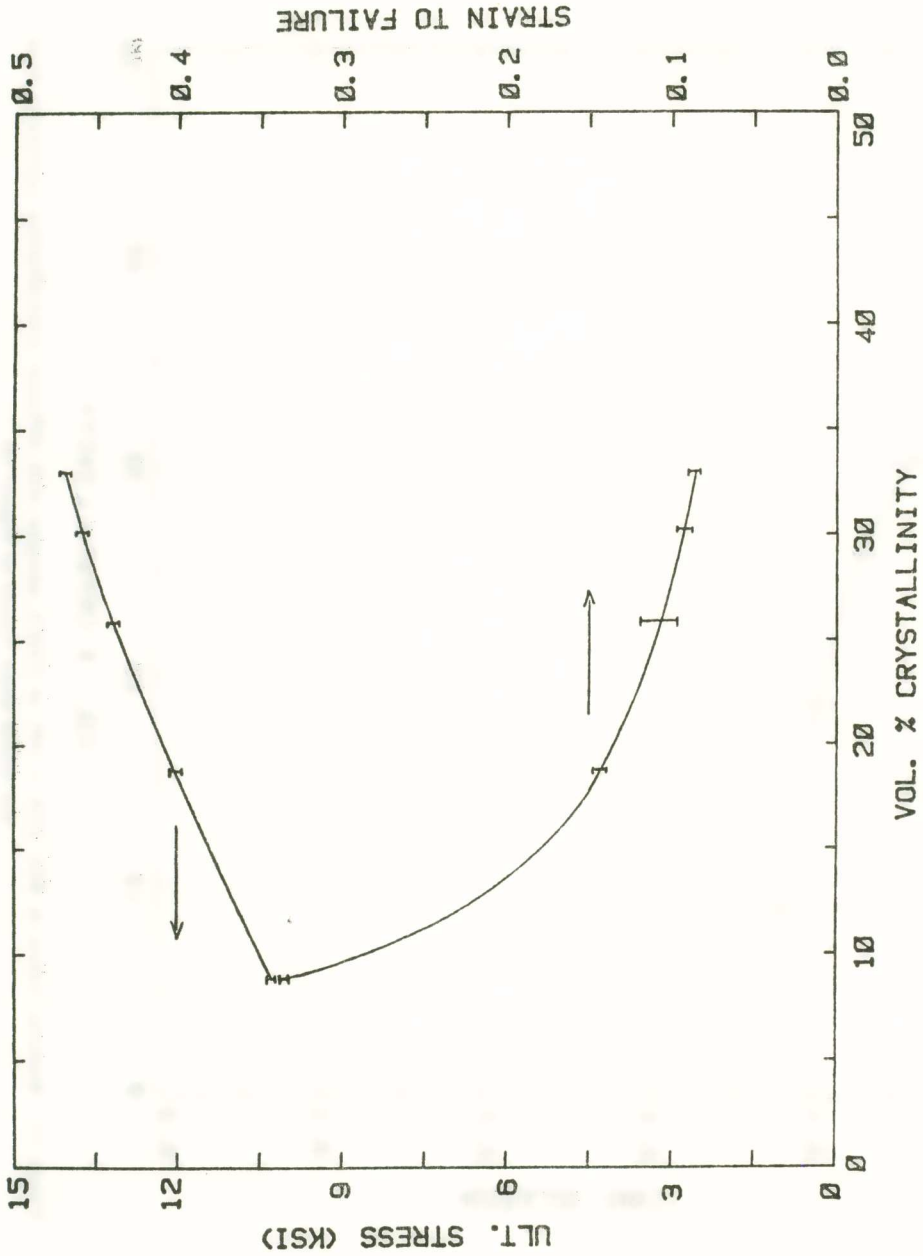


Figure 18. Ultimate stress values in KSI ($\text{PSI} \times 10^3$) and strain to failure values of PEEK samples with different crystallinities calculated from the curves of Figure 16.

(PEEK) polymer, both in its neat and in carbon fiber reinforced composite forms. Although part of a long-range fundamental study, these findings have provided a unique view of a novel polymer system that may play an important role in future technological developments of high performance composites.

Specifically, the work to date has made a breakthrough in processing studies with the new match die mold developed that is capable of cooling both neat polymer and composite samples at the phenomenal rate in excess of 115°C/sec; has also offered exciting possibilities in looking at the different morphologies produced by such process with edge grinding of sample and observing them under the polarizing microscope; has examined both physical and chemical modifications of the material while identifying, for the first time, the reaction of PEEK in the presence of copper and its plasticization and crystallization in methylene chloride. Finally, the coupling of processing, crystallinity, and environmental exposure were uniquely summarized with simple but revealing dynamic mechanical and stress-strain experiments bringing into focus also the mechanical behavior of the material.

Separately and collectively, these findings have identified several novel avenues for continued investigation that hold promise in increasing our basic understanding specifically for high performance polymer composites and crystalline polymers in general.

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Ὁ Ἀκαδημαϊκὸς κ. Περικλῆς Σ. Θεοχάρης προσθέτει τὰ ἑξῆς:

Ὁ καθηγητῆς κ. Δημ. Σεφέρης τοῦ Πανεπιστημίου Washington εἰς τὸ Seattle τῆς πολιτείας Washington τῶν ΗΠΑ εἶναι ἀπὸ τοὺς πρωτοπόρους χημικοὺς μηχανικοὺς ποὺ μελετοῦν τὴν συμπεριφορὰν τῶν πολυμερῶν καὶ τῶν συνθέτων τῶν ὑψηλῆς ἀντοχῆς καταλλήλων εἰς τὴν ἀεροπορικὴν βιομηχανίαν. Αἱ ἔρευναι τοῦ κ. Σε-

φέρη γίνονται πάντοτε σὲ στενή συνεργασία μὲ τὰς ἐφαρμογὰς εἰς τὴν βιομηχανίαν. Μεταξὺ τῶν μεγάλων βιομηχανιῶν μετὰ τῶν ὁποίων συνεργάζεται τὸ ἐργαστήριον ὑψηλῶν πολυμερῶν τοῦ Washington University εἶναι αἱ ἐταιρεῖαι κατασκευῆς ἀεροπλάνων Boeing καὶ Lockheed, ἡ ἐταιρεία πετρελαιοειδῶν Shell, ἡ χημικὴ βιομηχανία Dupont de Nemours, ἡ γαλλικὴ ἐταιρεία Rhone - Poulenc καὶ ἄλλαι.

Εἶχα τὴν εὐκαιρίαν νὰ γνωρίσω τὴν ἐπιστημονικὴ δραστηριότητα τοῦ συναδέλφου εἰς τὰς ΗΠΑ ἐπὶ τῇ εὐκαιρίᾳ τῆς ἀπονομῆς εἰς αὐτὸν τοῦ μεγάλου βραβείου δι' ἔρευνας τοῦ Προέδρου τῶν ΗΠΑ. Ὁ κ. Σεφέρης ἦτο μεταξὺ τῶν ὀλίγων νέων ἐπιστημόνων ποὺ ἔτυχον τῆς μεγάλης αὐτῆς διακρίσεως, ἡ ὁποία συνοδεύεται καὶ ἀπὸ ἔπαθλον 500.000 δολλαρίων δι' ἐνίσχυσιν τῶν ἐρευνῶν κλιμακούμενου σὲ πέντε συνεχῆ ἔτη.

Σήμερον αἱ βιομηχανίαι κατασκευῶν χρησιμοποιοῦν εὐρύτατα σύνθετα ὑλικά ἐξ ὑψηλῶν πολυμερῶν ὅπου λεπταὶ ἴνες ἐξ ἄνθρακος ἢ Kevlar^(R) ἀποχύνονται καὶ συνεργάζονται ἐντὸς μῆτρας ἐξ ὑψηλοῦ πολυμεροῦς ἢ ὁποία γενικῶς μέχρι σήμερον εἶναι ἡ ἐποξειδικὴ ρητίνη.

Διὰ τὴν βελτίωσιν τῆς συνεργασίας τῶν φάσεων συνθέτου ὑλικοῦ χρησιμοποιοῦνται σήμερον ἐποξειδικαὶ ρητίναι ὑψηλῆς ἀντοχῆς ἢ θερμοπλαστικαὶ ρητίναι εἰς τὰς μῆτρας τῶν συνθέτων ὑλικῶν. Τὰ ὑλικά αὐτὰ δίδουν καλυτέρας ιδιότητας εἰς τὰ σύνθετα ὑλικά, παρέχοντα ὑψηλοτέραν ἀντίστασιν εἰς τὴν διάδοσιν τῶν ρωγμῶν ὑψηλοτέρας τιμᾶς εἰς τὰς μηχανικὰς ιδιότητας τῶν ὑλικῶν κ.ἄ.

Ὁ κ. Σεφέρης ἐξετάζει τελευταίως εἰς τὸ ἐργαστήριόν του νέαν θερμοπλαστικὴν ρητίνην τὴν πολυ-αιθῆρ-αιθῆρ-κετόνην (PEEK) κατασκευαζομένην ἀπὸ τὴν ICI στὴν Ἀγγλίαν. Ἡ ρητίνη αὕτη εἶναι κρυσταλλικὸν πολυμερὲς ὑψηλοῦ σημείου τήξεως (385°C). Ἡ συμπεριφορὰ τοῦ πολυμεροῦς αὐτοῦ, ὅπως ἄλλωστε καὶ ὄλων τῶν ἄλλων πολυμερῶν, ἐπηρεάζεται ἀπὸ τὴν θερμοκρασίαν διαμορφώσεώς του καὶ τὴν θερμοκρασίαν χρήσεώς του.

Ὁ κ. Σεφέρης ἐφαρμόζοντας ἀναλυτικὰς μεθόδους, μελετᾷ τὴν δομὴν αὐτοῦ τοῦ ὑλικοῦ σὲ σχέσιν μὲ τὴν θερμικὴν του ἐπεξεργασίαν καὶ τὰς μηχανικὰς του ιδιότητας. Διὰ παρατηρήσεων εἰς τὸ μικροσκόπιον ἐπὶ λεπτῶν ἀποτμήσεων ἐκ τοῦ ὑλικοῦ τῆς μῆτρας ἢ καὶ τοῦ συνθέτου, παρασκευαζομένου εἰς θερμοκρασίαν ὑγροῦ ἀζώτου, κατάρθωσε νὰ παρατηρήσῃ τὴν σφαιρουλιτικὴν δομὴν τοῦ ὑλικοῦ.

Τελευταίως κατεσκεύασε χωανικὸν τύπον ταχείας ἀποψύξεως διὰ τὴν ἐπεξεργασίαν αὐτῶν τῶν ὑλικῶν ὑπὸ συνθῆκας ταχυτήτων ψύξεως ἀνερχομένων εἰς τοὺς 140°C/sec. Τροποποιώντας τὴν δομὴν τῶν δοκιμίων διὰ διαφόρων ταχυτήτων ἀποψύξεως κατάρθωσε νὰ διαπιστώσῃ διὰ πρώτην φορὰν ἀντιδράσεις τοῦ ὑλικοῦ μὲ τὸν χαλκὸν καὶ μὲ τὸ χλωριοῦχον μεθυλένιον. Δοκίμια μὲ μικροὺς σφαιρούλιτας ὅταν

έλθουν εις έπαφήν με χλωριοϋχον μεθυλένιον αλλάζουν την την κρυσταλλικήν των δομήν δίδοντας διαφορετικὰς ιδιότητες στο ύλικό. Η μελέτη του κ. Σεφέρη έχει προχωρήσει εις τό σημείον να προσδιορίζει πειραματικῶς και θεωρητικῶς τὰς ιδιότητας τῶν ύλικῶν αὐτῶν ἐν σχέσει πρὸς την δομήν των.

REFERENCES

1. J. C. Seferis and L. Nicolais Eds., *The Role of the Polymeric Matrix on Their Processing and Structural Properties of Composite Materials*, Plenum Press New York (1983).
3. J. D. Keenan, J. C. Seferis and J. T. Quinlivan, *J. Appl. Polym. Sci.* 24 2375 (1979).
3. W. J. Mikols and J. C. Seferis, ACS Symposium Series, 227 95 (1983).
4. H. S. Chu and J. C. Seferis, in *The Role of the Polymeric Matrix on Their Processing and Structural Properties of Composite Materials*, J. C. Seferis and L. Nicolais, Eds., Plenum Press New York, p. 53 (1983).
5. A. M. Ibrahim and J. C. Seferis, in *Interrelations between Processing Structure and Properties of Polymeric Materials*, J. C. Seferis and P. Theocaris, Eds., Elsevier Amsterdam, p. 325 (1984).
6. H. S. Chu and J. C. Seferis, *Polymer Composites* 5 124 (1984).
7. M. R. Duci, C. A. May and J. C. Seferis, ACS Symposium Series 227 304 (1983).
8. W. J. Mikols and J. C. Seferis, ACS Symposium Series, 132 293 (1980).
9. J. C. Seferis and R. J. Samuels, *Polym. Eng. and Sci.* 19 975 (1979).
10. A. R. Wedgewood and J. C. Seferis, *J. Pure and Appl. Chem.* 55 873 (1983).
11. A. R. Wedgewood and J. C. Seferis, *Polym. Eng. and Sci.* 24 328 (1984).
12. J. C. Seferis, A. E. Elia and A. R. Wedgewood, Proceedings European Meeting on Polymer Processing and Properties, Plenum New York, p. 423 (1983).
13. D. J. Blundell and B. N. Osborn, *Polymer* 24 953 (1983).
14. J. T. Hartness, *SAMPE Journal* 20 26 (1984).
15. H. E. Klei, "Thermal and Mechanical Characterization of Peek", Master's Thesis, J. C. Seferis, Director, Polymeric Composites Laboratory, University of Washington, Seattle, Washington (1984);
16. E. J. Stober, J. C. Seferis, and J. D. Keenan, *Polymer* 25 1845 (1984).
17. R. J. Samuels, *Structured Polymer Properties*, Wiley New York (1974).
18. P. C. Dawson and D. J. Blundell, *Polymer* 21 577 (1980).
19. F. N. Cogswell, Proceeding 28th National SAMPE Symposium, 28 528 (1983).